

Polymerizations in nonaqueous miniemulsions**Description**

- 5 The invention relates to a method of conducting polymerizations in nonaqueous miniemulsions.

10 Miniemulsion polymerization is an innovative process of heterophase polymerization which extends the use of conventional emulsion polymerization. Miniemulsions are dispersions of two substantially immiscible phases and, if desired, one or more surfactants, in which unusually small droplet sizes are realized. In the case of polymerization reactions in miniemulsions, an apolar

15 monomer or a mixture of monomers and, if desired, a cosurfactant are usually dispersed in water using a surfactant and high shear fields to form droplets of the desired order of magnitude, which are colloidally stabilized by the added surfactant (Sudol and El-Aasser in: Emulsion Polymerization and Emulsion Polymers; Lovell, P.A.; El-Aasser, M.S., ed., Chichester (1997), 699). In such miniemulsions, the droplet size may grow

20 further owing to collisions and fusions.

- 25 The German patent application 198 52 784.5-43 describes the osmotic stabilization of aqueous miniemulsions and microemulsions through the use of water-insoluble compounds as an emulsion-stabilizing component. By adding the water-insoluble substance to the oil phase,
- 30 which is normally the disperse phase of the emulsion, an osmotic pressure is built up which counteracts the capillary pressure or Kelvin pressure built up with the surface tension of the emulsion droplets. This has the consequence of preventing or retarding Ostwald ripening
- 35 of the emulsion droplets.

Nonaqueous dispersions are presently prepared primarily by inverse precipitation polymerization (Fengler and

10030033-032003

Reichert, Angew. Makromol. Chem. 225 (1995), 139),
inverse suspension polymerization (Lee and Hsu, J.
Appl. Polym. Sci. 69 (1998) 229; Omidian et al.,
Polymer 40 (1999), 1753) or inverse microemulsion
5 polymerization (Bicak and Sherrington, Reactive Funct.
Polym. 27 (1995), 155; Candau et al. J. Polym. Sci.,
Polym. Chem. Ed. 23 (1985), 193; Graillat et al., J.
Polym. Sci., Polym. Chem. 24 (1986), 427; Barton et
al., Angew. Makromol. Chem. 237 (1996) 99, Barton and
10 Stillhammerova, Angew. Makromol. Chem. 237 (1996),
113). In these cases, however, there is a change in
particle size and particle number during the
polymerization; in other words, mass transport via the
water phase determines the kinetics and the composition
15 of the polymers and polymer latices prepared.

Inorganic nanoparticles are likewise prepared by
reaction in inverse microemulsions (Pileni, Langmuir 13
(1997), 2366; Pileni, Supramol. Sci. 5 (1998), 321,
20 Pileni; Cryst. Res. Techn. 33 (1998), 1155; Adair et
al., Materials Sci. Eng. R 23 (1998), 139; Delfort et
al., J. Colloid Interf. Sci. 189 (1997), 151), although
the formulatability of an inverse microemulsion places
considerable restrictions with regard to synthesis
25 concentration and amount and nature of the surfactant.
Generally speaking, the mass flow density of such
inorganic particle syntheses is very low and at the
boundary of what is technically sensible.

30 Imhof and Pine (J. Colloid Interf. Sci. 192 (1997),
368) describe increasing the stability of nonaqueous
emulsions by adding small amounts of a water-insoluble
oil. The emulsions described therein, however, have an
average particle size of more than 1 μm , and so do not
35 constitute microemulsions or miniemulsions.

Surprisingly it has been found that miniemulsions may
also be formulated effectively in nonaqueous dispersion
media, where they lead to well-defined and stable

20030033 032300

polymer products in the form of latices. Here, for example, a polar monomer such as acrylic acid or hydroxyethyl metacrylate is introduced into an apolar solvent, e.g., a hydrocarbon such as hexadecane or cyclohexane, and is stabilized with a typical surfactant which for inverse systems has an HLB of preferably less than 7, such as Aerosol OT (sulfosuccinic acid bis-2-ethylhexyl ester sodium salt), Span[®]80 (sorbitan monooleate, Fluka) or KLE3729 (Goldschmidt), for instance. As an osmotically active reagent, moreover, use is made of a strong hydrophile such as water and/or a salt, examples being salts of the monomers such as sodium acrylate. In this way, osmotically stabilized microemulsions are obtained whose polymerization gives rise to inverse dispersions of polar polymers which can be used further directly but from which the polymer may also be isolated in a substantially water-free form. In comparison to the known inverse precipitation polymerization, the method of the invention has the advantage that the particle size of the dispersion is easier to adjust and that in the case of a copolymerization a more homogeneous polymer structure, and respectively a crosslinking density which can be adjusted easily and homogeneously, can be achieved. In comparison to inverse suspension polymerization, much smaller particles can be prepared.

Polar organic solvents such as formamide, dimethylacetamide or glycols may also be used as dispersion media for preparing miniemulsions in which hydrophobic substances, e.g., polymerizable monomers, may be dispersed. Here again, use is made of surfactants having an HLB, preferred for O/W systems, of more than 7, such as sodium dodecyl sulfate, for instance, and of an osmotic control reagent, in this case a hydrophobic substance. In this way, even water-sensitive monomers may be polymerized in dispersion, examples being methacryloyl chloride, ketimines, or monomers containing isocyanate and epoxide. The

resulting functional polymer products constitute important intermediates for the synthesis of further polymer products.

5 Inorganic polymerizations, as well, may be guided very advantageously in miniemulsions in organic nonaqueous media. Products obtained include inorganic polymers, glasslike nanoparticles or nanocrystals. Either an inverse or a reverse route may be chosen. In the case
10 of the inverse synthesis route, aqueous solutions of inorganic - e.g., metallic - precursors are miniemulsified in hydrophobic organic solvents, the coreactant then being added by way of the continuous phase or admixed in the form of a second miniemulsion.
15 In the case of the reverse synthesis route, a hydrophobic inorganic precursor, e.g., an organometallic compound, such as titanium tetraisobutoxide, is miniemulsified in a strongly polar organic solvent using a surfactant and an osmotic
20 control substance, e.g., an ultrahydrophobic compound; any residual solubility of the precursor in the continuous phase is of minor significance. By adding a further coreactant, e.g., water, by way of the continuous phase, or in the form of a second
25 miniemulsion, the polymerization is then initiated and leads to dispersed nanoparticles of controlled size and morphology.

The end products obtained are inorganic nanoparticles,
30 with a considerably higher space-time yield than in the prior art. Furthermore, it is also possible to obtain particles which could not be prepared hitherto owing to the lack of corresponding stable emulsion systems in the prior art.

35

The invention therefore firstly provides a method of conducting polymerizations in nonaqueous miniemulsions which is characterized in that an emulsion of reactants of a polymerization is produced in a nonaqueous fluid

dispersing medium, using a surfactant and an osmotically stabilizing component, and is reacted to give a dispersion of particles of the polymerization product in the medium.

5

Polymerizations in the sense of the present invention are reactions in which monomers or mixtures of monomers are reacted to polymers. One example of polymerizations are addition polymerizations, i.e., polymerizations which proceed steplessly without elimination of byproducts, examples being the preparation of acrylic and/or styrene polymers or copolymers of corresponding monomers or monomer mixtures.

15 Another example of polymerizations are polyaddition reactions, which proceed in stages without the elimination of byproducts, examples being the preparation of polyurethanes from polyfunctional hydroxy compounds and polyfunctional isocyanates, the preparation of polyureas from polyfunctional amines and polyfunctional isocyanates, and the preparation of polyepoxides from polyfunctional epoxides and polyfunctional amines, thiols and/or hydroxy compounds.

25 The polymerizations also include polycondensation reactions, which proceed in stages with elimination of byproducts, an example being unipolycondensations, which proceed with the participation of a single monomer, e.g., a hydroxycarboxylic acid or an amino acid, or in which two different monomers are involved, an example being the preparation of polyamides from polyfunctional carboxylic acids and polyfunctional amines or the preparation of polyesters from polyfunctional carboxylic acids and polyfunctional hydroxy compounds. Another example of polycondensation reactions are copolycondensations, in which more than two different monomers are involved. Other polymers too may be prepared by polycondensation from the corresponding monomers, e.g., polyimides, poly-

carbonates, amino resins, phenolic resins, polysulfides or urea resins.

1 The miniemulsion in which the polymerization is
5 conducted may be prepared by using high shear yields,
e.g., by means of a rod-type ultrasonicator, a jet
dispenser or a microfluidizer. The emulsion droplets
are preferably situated within the order of magnitude
10 of from 20 to 1000 nm, in particular from 30 to 600 nm
average particle diameter. In one embodiment of the
invention, a miniemulsion is formed from a disperse
phase of polar organic monomers in a continuous apolar
organic phase which is substantially miscible with the
15 polar phase. In this embodiment, the osmotically
stabilizing components used comprise hydrophilic
substances, especially water and/or salts, including
salts of the polar monomers, e.g., salts of acrylic
acid or methacrylic acid.

20 In another embodiment, a O/W miniemulsion is formed
from a disperse phase of apolar organic monomers in a
continuous polar organic phase, the two phases being
substantially immiscible. In this case, osmotically
stabilizing components used comprise hydrophobic
25 substances which mix with the apolar phase and have a
solubility in the polar phase of preferably less than 5×10^{-5} g/l, with particular preference less than 5×10^{-6} g/l, and most preferably less than 5×10^{-7} g/l at
room temperature. Examples thereof are hydrocarbons,
30 especially volatile, optionally halogenated
hydrocarbons, silanes, organosilanes, siloxanes, long-
chain esters, oils such as vegetable oils, e.g., olive
oil, hydrophobic dye molecules, blocked isocyanates,
and also oligomeric addition polymerization,
35 polycondensation, and polyaddition products.

The osmotically stabilizing components are added
generally in an amount of from 0.1 to 40% by weight,
preferably from 0.2 to 10% by weight, and with

particular preference from 0.5 to 5% by weight, based on the overall weight of the emulsion.

Also added for the purpose of stabilizing the O/W emulsion are surfactants such as sodium dodecyl sulfate, cetyltrimethylammonium chloride or else polymeric surfactants, such as block copolymers of styrene and ethylene oxide, for example. The amount of surfactant is preferably in the range from 0.1 to 20% by weight, more preferably from 0.2 to 10% by weight, with particular preference from 0.5 to 5% by weight, based on the overall weight of the emulsion.

The surfactants and osmotically stabilizing components are preferably selected so as to be compatible with the resultant polymerization product. Thus it is possible to use substances which possess a high volatility and/or which are usefully employed in the context of any further use of the polymeric dispersion, e.g., as plasticizers, dye, etc., so that they may contribute positively to the target application. By varying the surfactants and/or the osmotically stabilizing components and/or their amounts in the reaction batch it is possible to adjust as desired the particle size of the emulsion and of the resultant polymer dispersion.

The polymerization of the miniemulsion may also be initiated in a known way; for example, by adding a catalyst - a free-radical initiator, for example - and by raising the temperature. In this case, the preferred starting point is a critically stabilized emulsion, and with particular preference a thermodynamically stable emulsion. In the case of emulsions stabilized osmotically in this way, it is possible to obtain dispersions of the polymerization product whose particle sizes has not altered undesirably relative to that of the reactants emulsion. The particles of the polymerization product have an average size of

10030033-032002

preferably from 10 to 1000 nm and with particular preference from 30 to 600 nm.

Furthermore, the method of the invention is also
5 suitable for preparing multiphase nanohybrid particles,
e.g., particles which comprise polymerization products
and - encapsulated therein - inert particulate solids,
e.g., inorganic materials such as metal colloids,
oxidic particles such as SiO_2 , TiO_2 , CaSO_4 , CaCO_3 , BaSO_4 ,
10 zeolites, iron oxides, ZnO , CoO , CrO_2 , ZrO_2 ,
fluoroapatites and hydroxyapatites, and fine carbon
black, or organic materials, such as colloidal dye
aggregates. The size of the particulate solids is
generally situated within the range from 0.5 to 400 nm,
15 preferably in the range from 1 to 250 nm, and with
particular preference in the range from 10 nm to
200 nm. The size of the emulsion droplets is tailored
to the size of the particulate solids that are to be
encapsulated.

20 With polymerization reactions in osmotically stabilized
nonaqueous miniemulsions, it is possible to achieve
efficient embedding of particulate solids into the
shell of polymerization products. Preferably at least
25 60%, with particular preference at least 80%, more
preferably still at least 90%, and most preferably at
least 95% of the particulate solids are embedded. The
dispersions obtained by polymerization may be filmed
homogeneously, with the resultant films exhibiting high
30 mechanical stability and acid resistance. Owing to the
homogeneous encapsulation, the resultant nanohybrid
particles may be used, for example, for paints or
coatings with a high coloristic efficiency.

35 The invention further provides a method of conducting
inorganic polymerizations in nonaqueous miniemulsions
which is characterized in that a miniemulsion of at
least one of the reactants of an inorganic
polymerization is produced and is reacted.

An inorganic polymerization in the sense of the present invention is a polymerization in which at least one inorganic reactant is used and/or one inorganic reaction product is obtained. Examples of such inorganic polymerizations are the preparation of metal salt particles, metal oxide particles or metal sulfide particles.

10 In one embodiment of the method, a miniemulsion is formed from a disperse phase of an apolar reactant in a continuous polar organic phase, e.g., formamide, dimethylformamide, dimethylacetamide and/or dimethyl sulfoxide. The polymerization is then initiated by adding one or more further reactants by way of the continuous phase and/or in the form of a second miniemulsion. One example of this embodiment is the preparation of metal oxide particles from organometallic precursor compounds and water, in which water can be added by way of the continuous phase.

In another embodiment of the invention, an aqueous or nonaqueous miniemulsion is formed from a disperse phase of a polar reactant in a continuous apolar organic phase which is substantially immiscible with the disperse phase. Here again, the polymerization may be initiated by adding one or more further reactants by way of the continuous phase and/or in the form of a second miniemulsion. An example of this embodiment is the preparation of metal sulfide particles in which a miniemulsion of an aqueous solution of polar precursors, e.g., metal salts, in an apolar organic phase is produced, then a second miniemulsion containing sulfide ions is added, and these miniemulsions are mixed by applying corresponding shear fields and stimulated to undergo droplet exchange.

In the conduct of inorganic polymerizations, it is preferred to add surfactants and/or osmotically

stabilizing components (in the amounts indicated before) in order to stabilize the miniemulsions. The other preferred features in the context of the above-described organic polymerizations, as well, are transferable to the conduct of inorganic polymerizations.

Furthermore, the invention is to be illustrated by means of the following figures and examples:

10 Figure 1 shows an electron micrograph of PbS particles prepared by the method of the invention,

15 Figures 2 and 3 show electron micrographs of BaSO₄ particles prepared by the method of the invention, immediately following their formation (Fig. 2) and after 6-day maturation (Fig. 3).

20 **Example**

Example 1

25 1 g of acrylic acid was admixed with 60 mg of water and added to a solution of 9 g of cyclohexane and 250 mg of the surfactant KLE3729 (Goldschmidt AG). After the mixture had been stirred for 1 h at the highest magnetic stirrer setting, it was miniemulsified using a
30 rod-type ultrasonicator (Branson Sonifier, W400 Digital, Amplitude of 70%) for 60 s. The miniemulsion was heated to 65°C and the polymerization was initiated with 50 mg of azobisisobutyronitrile (AIBN). After 12 h, complete conversion was reached.

35 The particle size was measured using a Nicomp Particle Sizer (Model 370, PSS, Santa Barbara, USA) at a fixed scatter angle of 90°. The molecular weights of the polymers were determined by means of GPC analysis,

carried out using a P1000 pump and a UV1000 detector (Thermo Separation Products) at a wavelength of 260 nm with 5 μ m 8x300 mm SDV columns with 10^6 , 10^5 , and 10^3 angströms respectively (Polymer Standard Service) in
5 THF with a flow rate of 1 ml/min at 30°C. The molecular weights were calculated on the basis of a calibration relative to the standards.

Electron micrographs were taken using a Zeiss 912 Omega
10 electron microscope at 100 kV. The diluted particle dispersions were applied to a 400 mesh carbon coated copper grid and left to dry.

The average particle size of the resulting dispersion
15 was approximately 50 nm.

Example 2

In accordance with the instructions of example 1,
20 acrylic acid to which diethylene glycol diacrylate (DEGDA) had been added (degree of crosslinking 1:40) was polymerized. Here again, stable particles in the form of hydrogels were obtained.

25 The result of this experiment is shown in table 1.

Example 3

Instead of cyclohexane, hexadecane was used as the
30 dispersion medium. In accordance with the instructions described in example 1, dispersions were prepared.

The result of this experiment is shown in table 1.

Example 4

The amount of surfactant in example 3 was varied. It was possible to formulate stable inverse miniemulsions in the range from 2 to 100 w% surfactant, preferably

from 10 to 50 w% surfactant. The indication of the amount of surfactant in "w%" refers to the weight of the monomer and, respectively, of the resulting polymer.

5

The results are shown in table 1.

Example 5

10 Instead of KLE3927, the surfactants Span 80, C₁₈E₁₀, and AOT were used. Here too, it was possible to obtain polymer dispersions.

Example 6

15

Instead of acrylic acid, other hydrophilic monomers such as hydroxymethyl methacrylate (HEMA), acrylamide, and isopropylacrylamide, for instance, were polymerized.

20

a) 3 g of hydroxymethyl methacrylate were admixed with 125 mg of water, added to a solution of 25 g of cyclohexane and 300 mg of the surfactant KLE3729, and stirred for 1 h at the highest magnetic stirrer setting. In accordance with the instructions described in example 1, a miniemulsion was prepared and reacted. The particle size of the resulting polymer dispersion was approximately 130 nm (see table 2).

25

30

b) 3 g of acrylamide or isopropylacrylamide were admixed with 4 mg of water, added to a solution of 32 g of cyclohexane or hexane, respectively, and 500 mg of the surfactant KLE3729, and stirred for 1 h at the highest magnetic stirrer setting. In accordance with the instructions described in example 1, a miniemulsion was prepared and reacted. The particle size of the resulting dispersion was approximately 90 nm (see table 2).

35

It was also possible to produce dispersions following variation of the dispersing media, surfactants, surfactant amounts, and the initiator (see table 2).

5

Example 7

6 g of styrene and 250 mg of hexadecane (HD) were added to a solution of 24 ml of formamide and 72 mg of sodium dodecyl sulfate and mixed for 1 h with the magnetic stirrer setting on full. Using a rod-type ultrasonicator (1 min, amplitude of 90%), a miniemulsion was prepared. The polymerization was conducted at 72°C using 120 mg of $K_2S_2O_8$ (KPS) as initiator. After 6 h, the reaction was at an end. Highly stable polymer dispersions in the formamide organic medium were obtained.

When the amount of surfactant was increased to up to 500 mg it was found that the particle size can be adjusted by way of the amount of surfactant.

When using the nonionic surfactant Lutensol AT50 (amounts 125-1000 mg), it was also possible to produce stable polymer dispersions having particle sizes of between 70 and 250 nm.

The results are shown in table 3.

30 Example 8

Instead of formamide, glycol is used as the dispersion medium. Otherwise, the procedure described in example 7 was followed. Stable dispersions were obtained which had a much larger particle size than the corresponding formamide dispersions.

The results are shown in table 4.

Example 9

Hydrolysis-sensitive monomer substances such as glyceryl methacrylate, for example, were polymerized in accordance with the instructions described in example 7.

Example 10

In accordance with the instructions described in example 7, a polymer dispersion was prepared in dimethylacetamide (DMA).

Example 11

1 g of titanium(IV) isopropoxide was added to a solution of 10 ml of formamide and 130 mg of Lutensol AT50 and mixed for 1 h with the magnetic stirrer setting on full. Using a rod-type ultrasonicator (1 min, amplitude of 90%), a miniemulsion was prepared. By careful addition of a 10% strength aqueous formamide solution, stable TiO_2 dispersions were prepared.

Example 12

Two miniemulsions were formulated, with one miniemulsion containing droplets with heavy metal salts, e.g., Pb, Zn or Cd salts, in the form of acetates, for example, and the other miniemulsion containing droplets with Na_2S . After mixing, the systems were subjected to shearing, and stable metal sulfide dispersions were obtained.

1. Preparation of a PbS dispersion

1st miniemulsion: 270 mg of PbNO_3 were dissolved in 1 ml of water (final concentration 1 M). The salt solution was added to a mixture of 125 mg of surfactant (KLE3729 or Span[®]80) and 10 g of cyclohexane and stirred for an

hour at the highest magnetic stirrer setting. Miniemulsification was carried out using a rod-type ultrasonicator (Branson Sonifier, W400 Digital, amplitude of 70%) for 60 s.

5

2nd miniemulsion: 238 mg of Na_2S were dissolved in 1 ml of water (final concentration 2 M). The salt solution was added to a mixture of 125 mg of surfactant (KLE3729 or Span®80) and 10 g of cyclohexane and stirred for an hour at the highest magnetic stirrer setting. Miniemulsification was carried out using a rod-type ultrasonicator (Branson Sonifier, W400 Digital, amplitude of 70%) for 60 s.

10

The two miniemulsions were combined and treated with ultrasound for 60 s. The particle size was approximately 130 nm when using KLE3729 and approximately 50 nm when using Span 80. Fig. 1 shows the PbS particles when using KLE3729.

20

2. Preparation of a BaSO_4 dispersion

1st miniemulsion: 37.5 mg of BaCl_2 were dissolved in 1.5 ml of water (final concentration 0.1 M). The salt solution was added to a mixture of 250 mg of surfactant (Aerosol OT or Span®80) and 6 g of cyclohexane and stirred for an hour at the highest magnetic stirrer setting. Miniemulsification was carried out using a rod-type ultrasonicator (Branson Sonifier, W400 Digital, amplitude of 70%) for 60 s.

25

30

2nd miniemulsion: 21 mg of Na_2SO_4 were dissolved in 1.5 ml of water (final concentration 0.1 M). The salt solution was added to a mixture of 250 mg of surfactant (Aerosol OT or Span®80) and 6 g of cyclohexane and stirred for an hour at the highest magnetic stirrer setting. Miniemulsification was carried out using a rod-type ultrasonicator (Branson Sonifier, W400 Digital, amplitude of 70%) for 60 s.

35

2003-03-11

Table 1:

Monomer		Continuous phase		Emulsifier		Hydrophobe/ hydrophile		Initiator		Particle size (nm)
Acrylic acid	1 g	HD*	9 g	KLE3729	500 mg	H ₂ O	60 mg	AIBN	40 mg	58
Acrylic acid + DEGDA*	1 g	HD	9 g	KLE3729	500 mg	H ₂ O	58 mg	AIBN	51 mg	53
Acrylic acid + DEGDA	1 g	HD	9 g	KLE3729	254 mg	H ₂ O	78 mg	AIBN	52 mg	50
Acrylic acid + DEGDA	1 g	HD	10 g	KLE3729	127 mg	H ₂ O	85 mg	AIBN	50 mg	78
Acrylic acid + DEGDA	1 g	CH*	11 g	KLE3729	126 mg	H ₂ O	72 mg	AIBN	50 mg	78
Acrylic acid + DEGDA	1 g	CH	9 g	KLE3729	253 mg	H ₂ O	76 mg	AIBN	50 mg	50

*HD: Hexadecane; CH: cyclohexane, DEGDA: diethylene glycol diacrylate (molar ratio 1:80)

Table 2

Monomer		Continuous phase		Emulsifier		Hydrophobe/hydrophile		Initiator		Particle size (nm)
Acrylamide in H ₂ O	3 g	Hexane	32 g	Span80	513 mg			AIBN in hexane	80 mg	85/265
	4 g							5 ml		
Acrylamide in H ₂ O	3 g	CH	32 g	KLE3729	500 mg			AIBN in CH	100 mg	91
	4 g									
Acrylamide in H ₂ O	3 g	CH	32 g	KLE3729	250 mg			AIBN in CH	100 mg	101
	4 g									
Acrylamide in H ₂ O	3 g	CH	32 g	KLE3729	125 mg			AIBN in CH		138
	4 g									
Isopropyl-acrylamide in H ₂ O	1.5g	CH	32 g	KLE3729	500 mg			AIBN in CH		91
	7.5g									
HEMA	3 g	CH	25 g	KLE3729	300 mg	H ₂ O	125 mg	PEGA200	64 mg	129
HEMA	3 g	CH	25 g	KLE3729	500 mg	H ₂ O	125 mg	PEGA200	100 mg	102
HEMA	3 g	CH	25 g	KLE3729	500 mg	H ₂ O	125 mg	AIBN	60 mg	78
HEMA	2 g	HD	9 g	KLE3729	510 mg	H ₂ O	60 mg	PEGA200	108	84

CH: Cyclohexane, HD: Hexadecane; HEMA: Hydroxyethyl methacrylate

Table 3

Monomer		Continuous phase		Emulsifier		Hydrophobe/ hydrophile		Initiator		Particle size (nm)
Styrene	6 g	Formamide	24 ml	SDS	125 mg	HD*	250 mg	KPS*	120 mg	251
Styrene	6 g	Formamide	24 ml	Lutensol AT50	507 mg	HD*	266 mg	KPS	120 mg	71
Styrene	6 g	Formamide	24 ml	SDS	74 mg	HD	250 mg	KPS	120 mg	220
Styrene	6 g	Formamide	24 ml	SDS	252 mg	HD	270 mg	KPS	121 mg	183
Styrene	6 g	Formamide	24 ml	SDS	502 mg	HD	252 mg	KPS	121 mg	188
Styrene	6 g	Formamide	24 ml	Lutensol AT50	126 mg	HD	279 mg	KPS	120.5 mg	253
Styrene	6 g	Formamide	24 ml	Lutensol AT50	252 mg	HD	280 mg	KPS	120 mg	138

*HD: hexadecane; KPS: $K_2S_2O_8$

Table 4

Monomer		Continuous phase		Emulsifier		Hydrophobe/ hydrophile		Initiator		Particle size* (nm)
Styrene	6 g	glycol	27.6g	Lutensol AT50	503 mg	HD**	264 mg	KPS**	120 mg	386
Styrene	6 g	glycol	40 g	SDS	50 mg	HD	259 mg	KPS	122 mg	***
Styrene	6 g	glycol	40 g	SE3030	2 g	HD	261 mg	KPS	120 mg	144
Styrene	6 g	glycol	24 g	PEO/PPO	1 g	HD	250 mg	KPS in glycol	122 mg	104

* diluted with water

5 ** HD: hexadecane; KPS: $K_2S_2O_8$

*** not measured